

PATENT SPECIFICATION

(11) 1 404 969

1 404 969

(21) Application No. 59310/72 (22) Filed 22 Dec. 1972
 (31) Convention Application No. 2 200 127 (32) Filed 3 Jan. 1972 in
 (33) Germany (DT)
 (44) Complete Specification published 3 Sept. 1975
 (51) INT CL³ C07C 49/68
 (52) Index at acceptance

(19)



C2C 1231 1250 1372 1390 1394 1405 1416 1544 160X 213
 220 227 22X 22Y 247 250 251 252 255 256 25Y 280
 281 28X 313 31Y 337 338 342 34Y 351 352 353
 365 36G 368 36Y 386 387 388 43X 582 588 596
 633 635 638 63X 643 645 65X 662 668 699 760
 761 762 776 KW TT TY UA UB

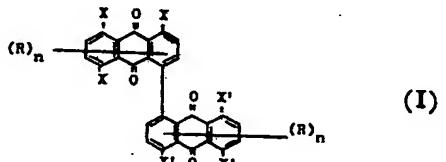
(54) PRODUCTION OF DICHLORO-1,1'-DIANTHRAQUINONYLS AND THEIR DERIVATIVES

(71) We, BADISCHE ANILIN- & SODA-FABRIK AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

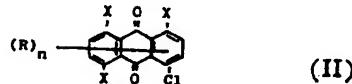
The present invention relates to a process for the production of α,α' -dichloro-1,1'-dianthraquinonyl derivatives from anthraquinone derivatives.

The production of 4,4'-dichloro-1,1'-dianthraquinonyl by reaction of 1,4-dichloro-anthraquinone in nitrobenzene in the presence of copper powder is described in "Monatshafe für Chemie", Band 39 (1918), Page 839. According to the author's report there resulted a brown, amorphous product, from which 4,4'-dichloro-1,1'-dianthraquinonyl could be isolated as a light brown product after a cumbersome and expensive purification operation. It is also stated in the same reference that the corresponding reaction, which is also characterised as an Ullmann reaction, does not occur with 1,5- and 1,8-dichloroanthraquinone.

We have now found that α,α' -dichloro-1,1'-dianthraquinonyls of the formula:—



in which one X and one X' each denote chlorine and the other X and X' denote hydrogen, chlorine or hydroxy, R denotes alkyl having one to four carbon atoms, a heterocyclic 5-membered ring with two hetero atoms, which can be condensed with a benzene ring, the —COOR¹ or the —CONR² R³ group, n denotes zero, one or two, R¹ denotes alkyl having one to four carbon atoms, R² denotes hydrogen or alkyl having one to four carbon atoms and R³ denotes alkyl having one to four carbon atoms or an optionally substituted phenyl radical, and in which one X and one X' together with the carbon atom of the neighbouring carbonyl group can form a condensed 6-membered carbocyclic ring or a 5- or 6-membered heterocyclic ring, can be produced in an advantageous manner by reacting dichloroanthraquinones of the formula:—



in which X, R and n are as defined above, in a strongly polar aprotic solvent which is miscible with water, or a mixture of such solvents, in the presence of at least an equimolar amount of copper powder.

[Price 33p]

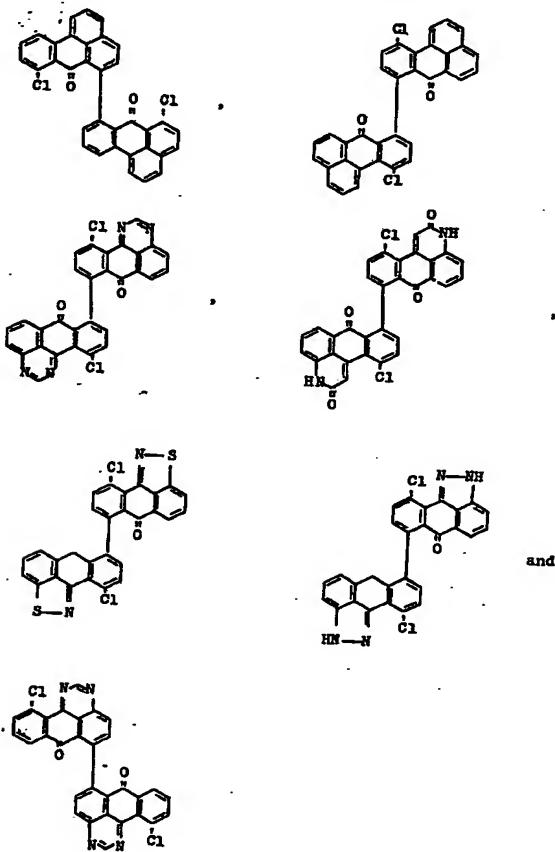
α,α' -Dichloro-1,1'-dianthraquinonyls of formula I can be obtained in high yield and good purity and simultaneously in high space-time yield according to the process of the present invention.

The following dichloroanthraquinones of formula II can for example be used:

5 1,4-dichloroanthraquinone, 1,5-dichloroanthraquinone, 1,8-dichloroanthraquinone, 1,4-dichloro-5,8-dihydroxyanthraquinone, 1,5-dichloro-4-hydroxyanthraquinone, 1,8-dichloro-4,5-dihydroxyanthraquinone, 5,8-dichlorobenzanthrone, 5,8-dichloro-1,9-anthrapyrimidine, 5,8-dichloro-1(N),9-anthrapyridone, 5,8-dichloro-1,9(N)-isothiazoloanthrone, 5,8-dichloro-1,9-pyrazoloanthrone, 4,5-dichloro-1,9-pyrazoloanthrone, 4,5-dichlorobenzanthrone, 4,8-dichloro-1,9-anthrapyrimidine, 1,4-dichloro-2-methylanthraquinone, 1,4-dichloro-6-methyl-anthraquinone, 1,4-dichloro-anthraquinone-6-carboxylic acid esters such as the methyl, ethyl, propyl and n- or iso-butyl esters, 1,4-dichloroanthraquinone-2-carboxylic acid esters such as the methyl, ethyl, propyl, and n- or iso-butyl esters, 1,4-dichloroanthraquinone-6-carboxylic amides such as the anilide or the N,N-dialkylamides, 1,4-dichloro-anthraquinone-2-carboxylic amides such as the anilide or the N,N-dialkyl amides, 1,4-dichloroanthraquinone derivatives which have a heterocyclic radical in the 2- or 6-position, for example 1,4-dichloro-2-[benzoxazolyl-(2)]-anthraquinone, 1,4-dichloro-2-[benzthiazolyl-(2)]-anthraquinone, 1,4-dichloro-6-[benzoxazolyl-(2)]-anthraquinone, 1,4-dichloro-2-[benzimidazolyl-(2)]-anthraquinone, 1,4-dichloro-6-[benzimidazolyl-(2)]-anthraquinone, 1,4-dichloro-6-[benzimidazolyl-(2)]-anthraquinone.

10 15 20

Reaction products of formula I include above all 4,4'-dichloro-1,1'-dianthraquinonyl, 5,5'-dichloro-1,1'-dianthraquinonyl and the compounds



These compounds are particularly suitable as starting materials for conversion to dyes. Correspondingly, particularly preferred starting compounds of formula II are 1,4-dichloroanthraquinone, 1,5-dichloroanthraquinone, 4,5-dichlorobenzanthrone, 5,8-di-

chlorobenzanthrone, 5,8-dichloro-1,9-anthrapyrimidine, 5,8-dichloro-1(N),9-anthrapyridone, 5,8-dichloro-1,9(N)-isothiazoloanthrone, 5,8-dichloro-1,9-pyrazoloanthrone and 4,8-dichloro-1,9-anthrapyrimidine.

5 Examples of strongly polar, aprotic solvents which are miscible with water are 5 dimethylsulphoxide, tetramethylenesulphone and the N,N-dialkyl carboxylic amides, for example N,N-dimethyl formamide, N,N-dimethylacetamide, N,N-dimethylpropionamide, N,N-diethylformamide, N,N-diethylacetamide, N,N-diethylpropionamide, N,N,N',N'-tetramethylurea, also the cyclic N,N-dialkyl carboxylic amides, for example 10 N-methylpyrrolidone, N-ethylpyrrolidone and N-methyl-caprolactam. On economic grounds dimethylsulphoxide, N,N-dimethylformamide, N-methylpyrrolidone and mixtures of two or more thereof are preferred as the strongly polar, aprotic solvent miscible 10 with water.

15 The reaction is generally carried out as follows: The dichloroanthraquinone of formula II is suspended or dissolved in the solvent or solvent mixture and the mixture is heated to the reaction temperature. At this temperature at least the equivalent amount or an excess of copper powder is added in such a way that the temperature in the reaction mixture is maintained constant without an additional supply of heat. In some cases, for example with 1,4-dichloroanthraquinone, the reaction proceeds so vigorously that the copper powder must be added in very small portions so that the reaction is not too violent. On the other hand, with dichloroanthraquinones that are slow to react, for example 1,5-dichloroanthraquinone, the total amount of the copper powder can be added at once to the hot solution. The reaction of dichloroanthraquinones (II) that are slow to react can be accelerated by the addition of catalytic amounts of copper (I) halides, for example copper (I) chloride or copper (I) bromide. By 20 catalytic amounts we mean amounts of 0.005 to 1 weight % based on the amount of copper used.

25 The amount of the water-miscible, strongly polar, aprotic solvent used is suitably from 0.5 to 10 times, preferably from 0.5 to 5 times, the amount of the dichloroanthraquinone compound (II) used, on a weight basis. The actual amount used depends on the particular compound. For example, it is observed in the reaction of 1,8-dichloroanthraquinone that the yield of 8,8'-di dichloro-1,1'-dianthraquinonyl falls sharply with the use of larger amounts of solvent. The elimination of a chlorine atom is found to occur as a side reaction instead of the formation of the dianthraquinonyl molecule. In other cases, however, the amount of solvent is not critical. The amount of solvent is kept as low as possible on economic grounds but should, however, be chosen such that the reaction mixture is stirrable throughout the whole reaction.

30 The reaction of the dichloroanthraquinone compounds (II) is carried out in general at from 70 to 200° C., preferably from 120 to 160° C.

35 The duration of the reaction is chiefly dependent on the dichloroanthraquinone compound (II) and the reaction temperature used. In general the reaction is complete after a period of from half an hour to five hours. If the reaction is carried out at a temperature in the range from 120 to 160° C. the reaction is complete in most cases after a period of from half an hour to two hours. The reaction product generally 40 crystallises out during the reaction and can be separated easily from the reaction mixture, after cooling, by filtration, centrifugation or decantation. In those cases where the dichloro-1,1'-dianthraquinonyl compound obtained is soluble in the solvent or solvent mixture, a solvent or diluent in which the reaction product is either insoluble or only slightly soluble is added to the reaction mixture and only then is the reaction product separated out. Solvents and diluents suitable for this purpose are for example 45 methanol, ethanol, propanol, acetic acid and, above all, water.

50 The reaction product can thereafter be freed in a conventional manner from the copper that may still be present, for example by treatment with sodium chlorate and hydrochloric acid or by treatment with hot dilute nitric acid. In this way the water-solubility of the residue of the solvent still remaining in the filtration residue is not affected.

55 The use of dimethylformamide as solvent for the Ullmann reaction for the production of substituted diphenyls and dinaphthyls has already been described in "J. Amer. Chem. Soc." Band 74 (1952), at page 5782. On the basis of this literature reference an expert ought to expect in the present case that, because the course of the Ullmann reaction has been made simpler, still higher polymeric anthraquinonyls would be formed by the reaction of 1,4-dichloroanthraquinone, as this is known to occur in the known conversion of 1,4-dichloroanthraquinone in boiling nitrobenzene in the presence of copper powder. It was therefore not to be expected that the corresponding α,α' -dichloro-1,1'-dianthraquinonyl would be obtained in excellent yield and purity using strongly polar, aprotic solvents miscible with water.

The reaction products are valuable starting materials for the production of dye-stuffs, particularly pigments, because the chlorine atoms in the α - and α' -positions can be substituted by other nucleophilic groups.

The invention is illustrated by the following Examples in which the parts and percentages are by weight unless otherwise stated. The parts by volume are related to the parts by weight in the same way as the litre to the kilogram.

Example 1.

277 Parts of 1,4-dichloroanthraquinone are introduced into 500 parts by volume of dimethylformamide. The mixture is heated to boiling point until a clear solution is attained. The heating is now stopped and 70 parts of copper powder are added in batches at 120° C. with stirring so that the exothermic reaction just continues in progress. Thereafter the mixture is stirred for a further one to two hours at 120° C., diluted with 250 parts by volume of acetic acid and filtered hot. The filter cake is washed with hot dimethylformamide and then with hot water, and then introduced into 500 parts by volume of approximately 30% nitric acid for decoppering. It is digested for one hour at 60 to 70° C., filtered and washed until neutral with hot water. After drying, 230 parts of 4,4'-dichloro-1,1'-dianthraquinonyl is obtained in the form of yellowish crystals (an amount corresponding to the calculated yield). Content of chlorine: calculated 14.7%, found 14.5%. The compound does not melt below 360° C.

10 277 Parts of 1,4-dichloroanthraquinone are introduced into 500 parts by volume of dimethylformamide. The mixture is heated to boiling point until a clear solution is attained. The heating is now stopped and 70 parts of copper powder are added in batches at 120° C. with stirring so that the exothermic reaction just continues in progress. Thereafter the mixture is stirred for a further one to two hours at 120° C., diluted with 250 parts by volume of acetic acid and filtered hot. The filter cake is washed with hot dimethylformamide and then with hot water, and then introduced into 500 parts by volume of approximately 30% nitric acid for decoppering. It is digested for one hour at 60 to 70° C., filtered and washed until neutral with hot water. After drying, 230 parts of 4,4'-dichloro-1,1'-dianthraquinonyl is obtained in the form of yellowish crystals (an amount corresponding to the calculated yield). Content of chlorine: calculated 14.7%, found 14.5%. The compound does not melt below 360° C.

Example 2.

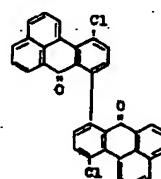
277 Parts of 1,4-dichloroanthraquinone are dissolved in 400 parts by volume of dimethylsulphoxide at 100° C. 0.05 parts of copper (I) chloride is added and then 67 parts of copper powder are added all at once so that the reaction remains in progress without heating. Then the reaction mixture is stirred for a further one hour at 120° C., diluted with 200 parts by volume of acetic acid and filtered at 80° C. It is thereafter washed with hot acetic acid and decoppered in the manner described in Example 1. After drying, 195 parts of 4,4'-dichloro-1,1'-dianthraquinonyl (corresponding to 81% of the calculated yield) are obtained. Content of chlorine: calculated 14.7%, found 14.5%.

20 30 If the dimethylsulphoxide is replaced in Example 2 by the same amount of the solvents named in the following Table, the results listed there are obtained.

Example	Solvent	Yield Parts	% Cl
3	N-methylpyrrolidone	189	14.9
4	N,N,N',N' -tetramethylurea	198	14.6
5	N,N-dimethylacetamide	218	14.7
6	N,N-diethylformamide	203	14.9
7	N-methylcaprolactam	199	14.4

Example 8.

35 299 Parts of 5,8-dichlorobenzanthrone and 0.5 parts of copper (I) chloride are stirred into 800 parts by volume of N-methylpyrrolidone at 130° C. 67.5 parts of copper powder are added thereto inside one hour and the mixture is then stirred for a further two hours at 140° C. The reaction mixture is poured into a 500 parts by volume of water, filtered and decoppered in the manner described in Example 1. After drying, 229 parts of dichloro-dibenzanthronyl of the formula



is obtained. After recrystallisation from dimethylformamide the compound melts at 332° C. and its chlorine content is 13.3% (calculated 13.5%).

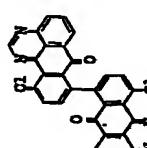
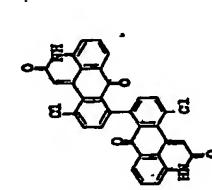
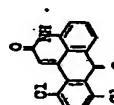
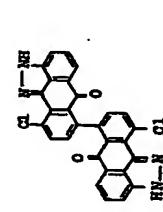
Example 9.

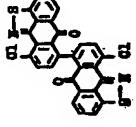
The procedure of Example 8 is repeated except that, instead of the 5,8-dichloro-5 benzanthrone, the same amount of 4,5-dichlorobenzanthrone is used. Yield: 196 parts of 5,5'-dichloro-4,4'-dibenzanthrone with a melting point of 300 to 303° C. and a chlorine content of 13.9%.

Examples 10 to 19.
In an analogous manner to Examples 1, 2 or 8 the $\alpha\alpha'$ -dichloro-1,1'-dianthra-10 quinonyl derivatives listed in the following Table are obtained.

Example	Starting material	Reaction product	Melting Point °C	Cl Calculated %	Cl Found %
10	1,5-dichloroanthraquinone	5,5'-dichloro-1,1'-dianthraquinonyl	>360	14.7	14.8
11	1,4-dichloro-2-methyl-1-anthraquinone	2,2-dimethyl[4-4'-dichloro-1,1'-dianthraquinonyl]	>360	13.9	13.5
12	1,4-dichloro-6-methyl-1-anthraquinone	4,4'-dichloro-6'-(7')-dimethyl-1,1'-dianthraquinonyl*)	>360	13.9	13.4
13	1,4-dichloro-5,8-dihydroxy-anthraquinone	4,4'-dichloro-5,8,5',8'-tetrahydroxy-1,1'-dianthraquinonyl	>360	13.0	12.7
14	1,4-dichloroanthraquinone-6-carboxylic anilide	4,4'-dichloro-1,1'-dianthraquinonyl-[6(7),6'(7')-dicarboxylic dianilide*)	>360	9.8	9.4
15	1,4-dichloro-6-benzoazolo-(2)-anthraquinone	4,4'-dichloro-6(7),6'(7')-bis-benzoazola-(2)-1,1'-dianthraquinonyl*)	>360	9.9	10.1

*) mixture of isomeric dianthraquinonyl compounds.

Example	Starting material	Reaction product	Melting Point °C	Cl calculated %	Cl found %
16			>350	13.4	13.0
17			>350	12.7	12.3
18			>350	14.0	14.2

Example	Starting material	Reaction product	Melting Point °C	Cl Calculated %	Cl found %
19			>350	13.1	13.7

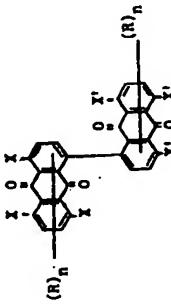
Example 20.

67.5 Parts of copper powder are added inside one hour at 150° C. to a melt of 277 parts of 1,8-dichloroanthraquinone, 160 parts by volume of dimethylformamide and 0.3 parts of copper (I) chloride. The reaction mixture is then stirred for a further two hours at 150 to 160° C. and then diluted with 400 parts by volume of acetic acid. The crystalline slurry is filtered at 75° C. and washed with hot glacial 5 7. 160 parts of 8,8'-dichloro-1,1'-dianthaquinone are obtained. Melting point 30Q— 10 305° C.; chlorine content: calculated 14.6%; found 14.5%.

With the use of larger quantities of dimethylformamide the yield of 8,8'-dichloro-1,1'-dianthaquinone falls sharply and 1-chloroanthraquinone is obtained in increasing quantities, i.e. splitting off of an α -chlorine atom occurs.

WHAT WE CLAIM IS:—

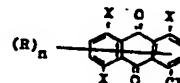
15 1. A process for the production of a dichloro-1,1'-dianthaquinone derivative of the formula:—



5 in which one X and one X' each denote chlorine and the other X and X' denote hydrogen, chlorine or hydroxy, R denotes alkyl having 1 to 4 carbon atoms, a heterocyclic 5-membered ring with two hetero atoms which can be condensed with a benzene ring, the $-\text{COOR}^1$ group or the $-\text{CONR}^2\text{R}^3$ group, n denotes the values zero, 1 or 2, R¹ denotes alkyl having 1 to 4 carbon atoms, R² denotes hydrogen or alkyl having 1 to 4 carbon atoms and R³ denotes alkyl having 1 to 4 carbon atoms or an optionally substituted phenyl radical, and in which one X and one X' together with the carbon atom of the neighbouring carbonyl group may form a 6-membered carbocyclic ring or a 5- or 6-membered heterocyclic ring, wherein a dichloroanthraquinone of the formula:—

5

10



15 in which X, R and n are as defined above, is reacted in a strongly polar, aprotic solvent which is miscible with water, or in a mixture of such solvents, in the presence of at least an equimolar quantity of copper powder.

15

20 2. A process as claimed in claim 1 wherein the solvent is dimethylsulphoxide, tetramethylenesulphone, N,N-dimethylformamide, N,N-dimethylacetamide, N,N-dimethylpropionamide, N,N-diethylformamide, N,N-diethylacetamide, N,N-diethylpropionamide, N,N,N',N'-tetramethylurea, N-methylpyrrolidone, N-ethylpyrrolidone or N-methylcaprolactam or a mixture of two or more thereof.

20

25 3. A process as claimed in claim 1 wherein the solvent is dimethylsulphoxide, N,N-dimethylformamide, N-methylpyrrolidone or a mixture of two or more thereof.

20

4. A process as claimed in any of claims 1 to 3 wherein the solvent is employed out in an amount of from 0.5 to 10 parts by weight per part by weight of the dichloroanthraquinone compound.

25

30 5. A process according to any of claims 1 to 4 wherein the α,α -dichloroanthraquinone is 1,4-dichloroanthraquinone, 1,5-dichloroanthraquinone, 4,5-dichlorobenzanthrone, 5,8-dichlorobenzanthrone, 5,8-dichloro-1,9-anthrapyrimidine, 5,8-dichloro-1(N),9-anthrapyridone, 5,8-dichloro-1,9(N)-isothiazoloanthrone, 5,8-dichloro-1,9-pyrazoloanthrone or 4,8-dichloro-1,9-anthrapyrimidine.

30

35 6. A process as claimed in any of claims 1 to 5 wherein the reaction is carried out at a temperature of from 70 to 200° C.

35

7. A process as claimed in claim 6 wherein the reaction is carried out at a temperature in the range from 120 to 160° C.

8. A process as claimed in any of claims 1 to 7 wherein the reaction is carried out in the presence of a catalytic amount of copper (I) chloride or copper (I) bromide.

35

9. A process as claimed in claim 1 and substantially as hereinbefore described in any one of the foregoing Examples.

10. A dichloro-1,1'-dianthraquinonyl derivative when produced by a process as claimed in any of claims 1 to 9.

J. Y. & G. W. JOHNSON,
Furnival House, 14—18, High Holborn, London, WC1V 6DE,
Chartered Patent Agents,
Agents for the Applicants.